FAVORABLE ATTRIBUTES OF ALKALINE/ SURFACTANT/POLYMER FLOODING[1]

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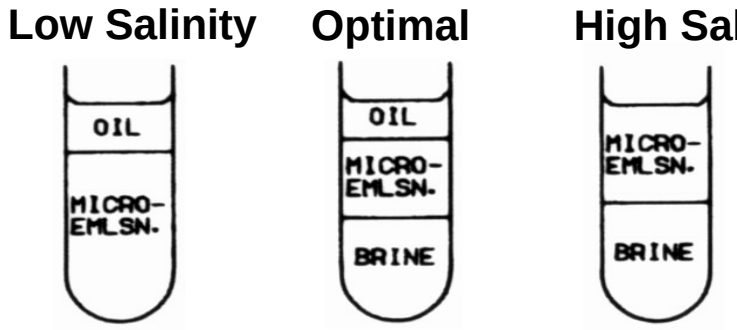
[1]**Supported by DOE grant DE-FC26-03NT15406 and the Rice Consortium on Processes in Porous Media**

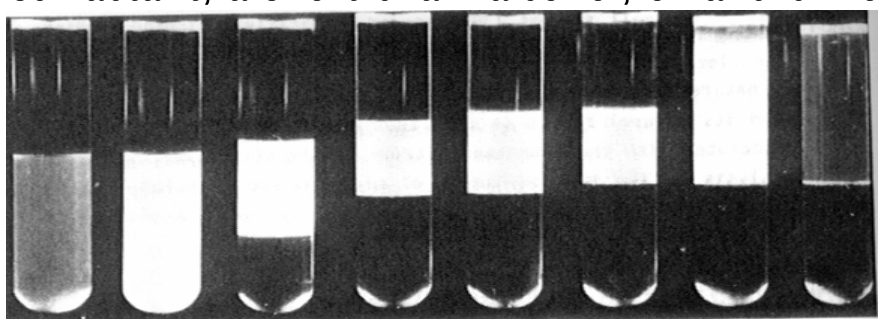
[2]**Now with Halliburton, Duncan, OK**

Phase Behavior and Interfacial Tension for Anionic Surfactants



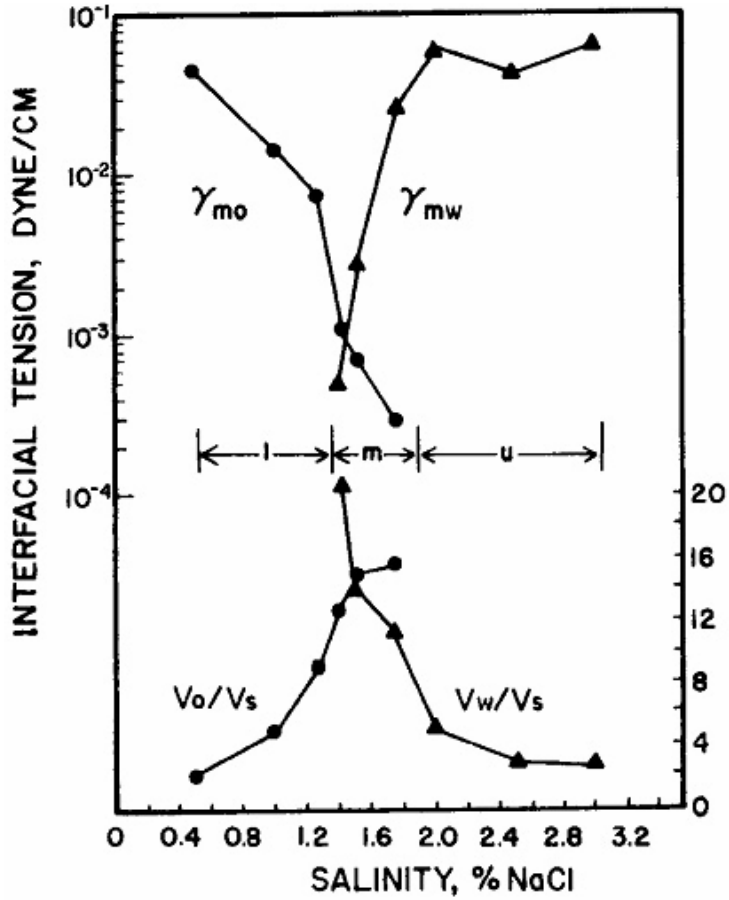
(Healy et al, 1976)

System containing a petroleum sulfonate surfactant, a short-chain alcohol, oil and brine



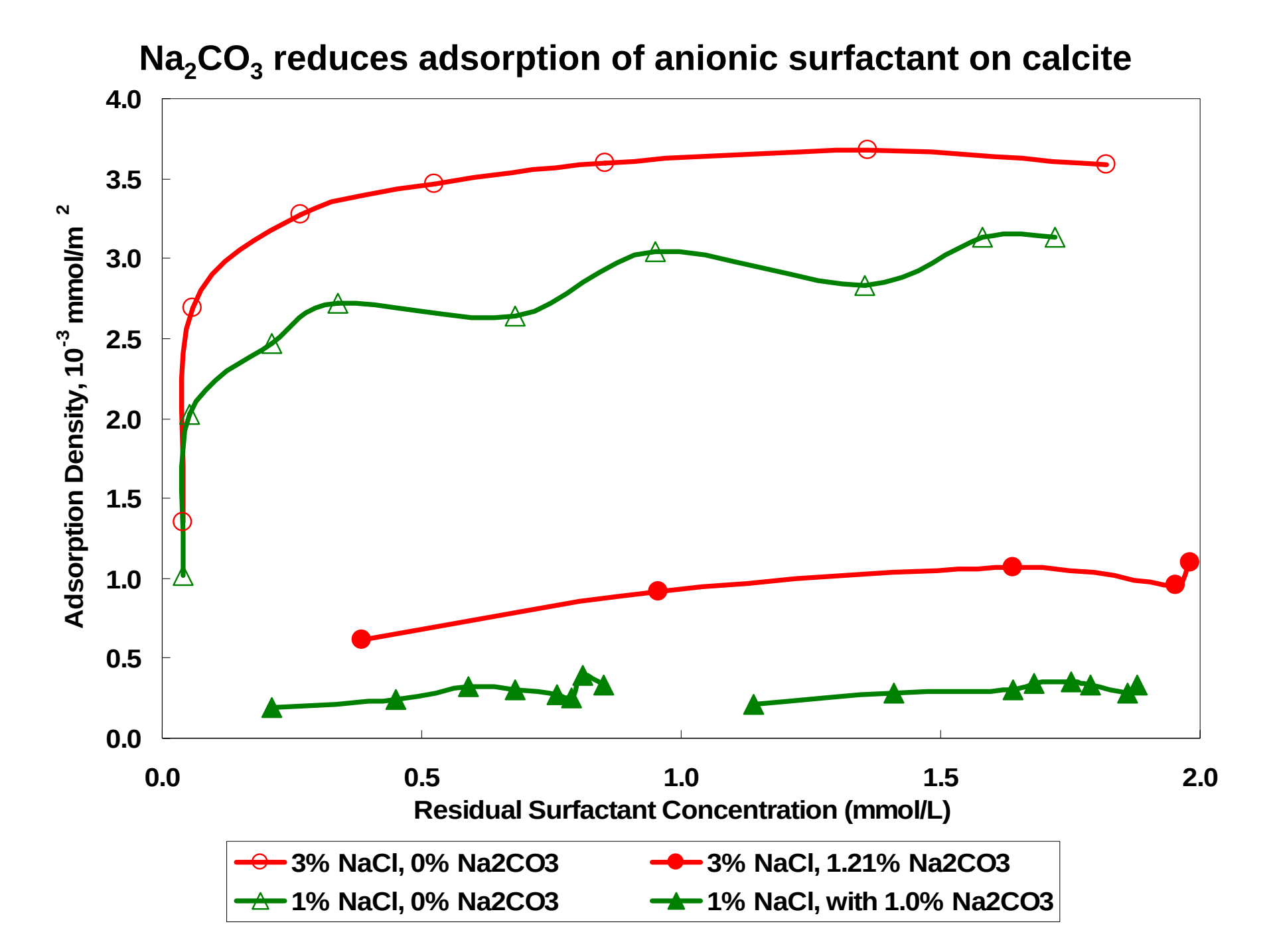
NaCl concentration increases ⟶

3% 63/37 MEAC$_{12}$OXS/TAA
48.5% 90/10 I/H, 48.5% X% NaCl

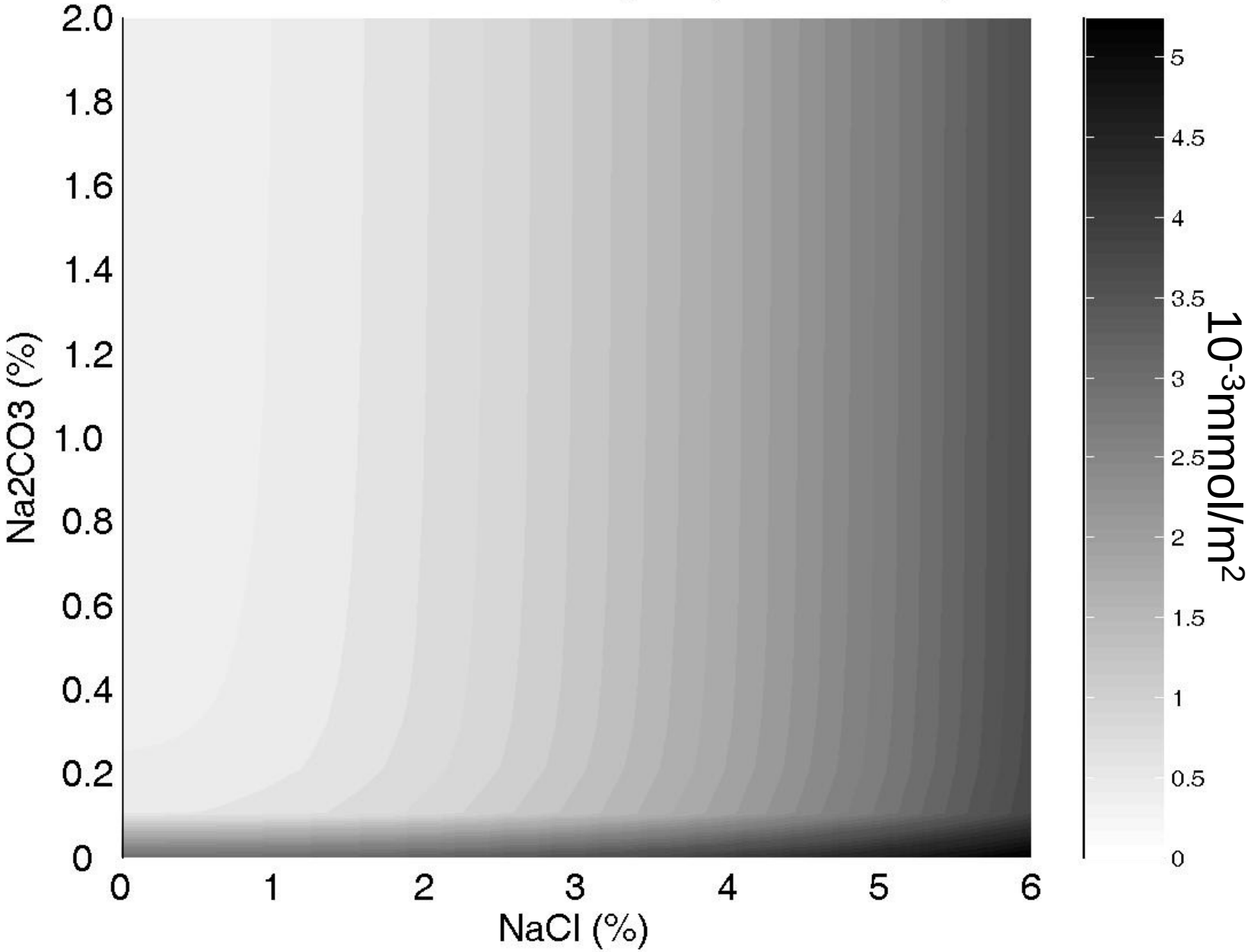


ANIONIC SURFACTANT ADSORPTION IN ALKALINE/SURFACTANT PROCESSES

- **Sandstone Formations**
  - **Reduced adsorption due to reversal of positively charged sites on clays at high pH**
- **Carbonate Formations**
  - **Carbonate ion is potential determining ion for calcite and dolomite; makes mineral surface negatively charged even at neutral pH, where it is typically positive**
  - **Reduced adsorption of anionic surfactant in presence Na_2CO_3 (but not NaOH)**
  - **For W. Texas dolomite core, reduction from 0.5 to 0.04 mg/g expected at 1% NaCl based on BET area and data of next slide**


Na2CO3 reduces adsorption of anionic surfactant on calcite
Adsorption Density, 10-3 mmol/m2
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
Residual Surfactant Concentration (mmol/L)
3% NaCl, 0% Na2CO3
3% NaCl, 1.21% Na2CO3
1% NaCl, 0% Na2CO3
1% NaCl, with 1.0% Na2CO3

Contour of plateau adsorption for N67 IOS(4:1) on calcite



FIELD EXPERIENCE WITH ALKALINE/SURFACTANT PROCESSES

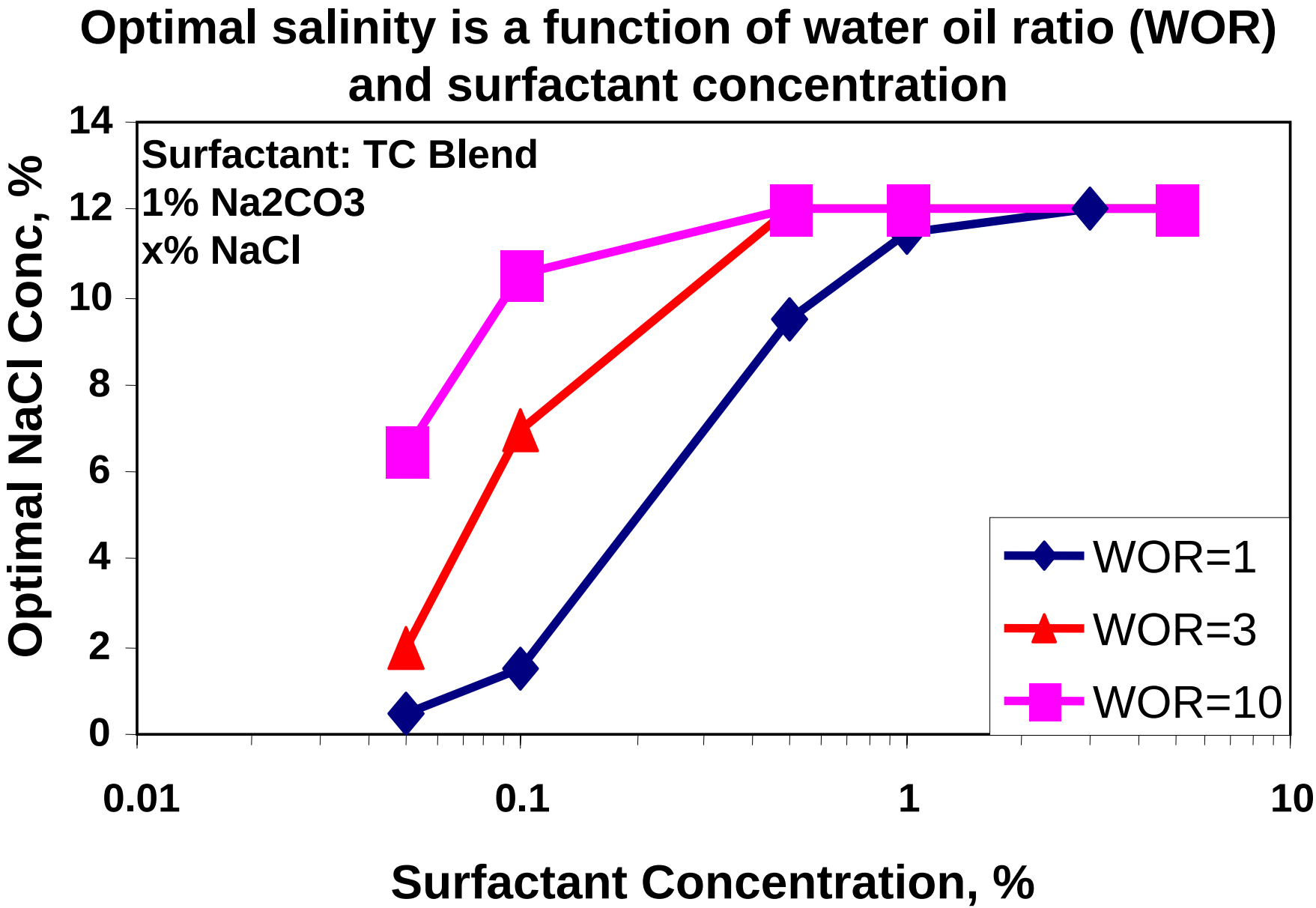
- **Shell pilot test (Louisiana, 1980s): Good microscopic displacement efficiency but poor sweep since no polymer**
- **Surtek: Several ASP projects (with polymer) over past several years; improved recovery; work ongoing**
- **China: Approx. 10 pilot ASP tests, most at Daqing including one with 17 injectors and 27 producers; incremental recovery of order 20-25% OOIP for those currently complete; work ongoing**

ASP: TWO SURFACTANTS FROM DIFFERENT SOURCES

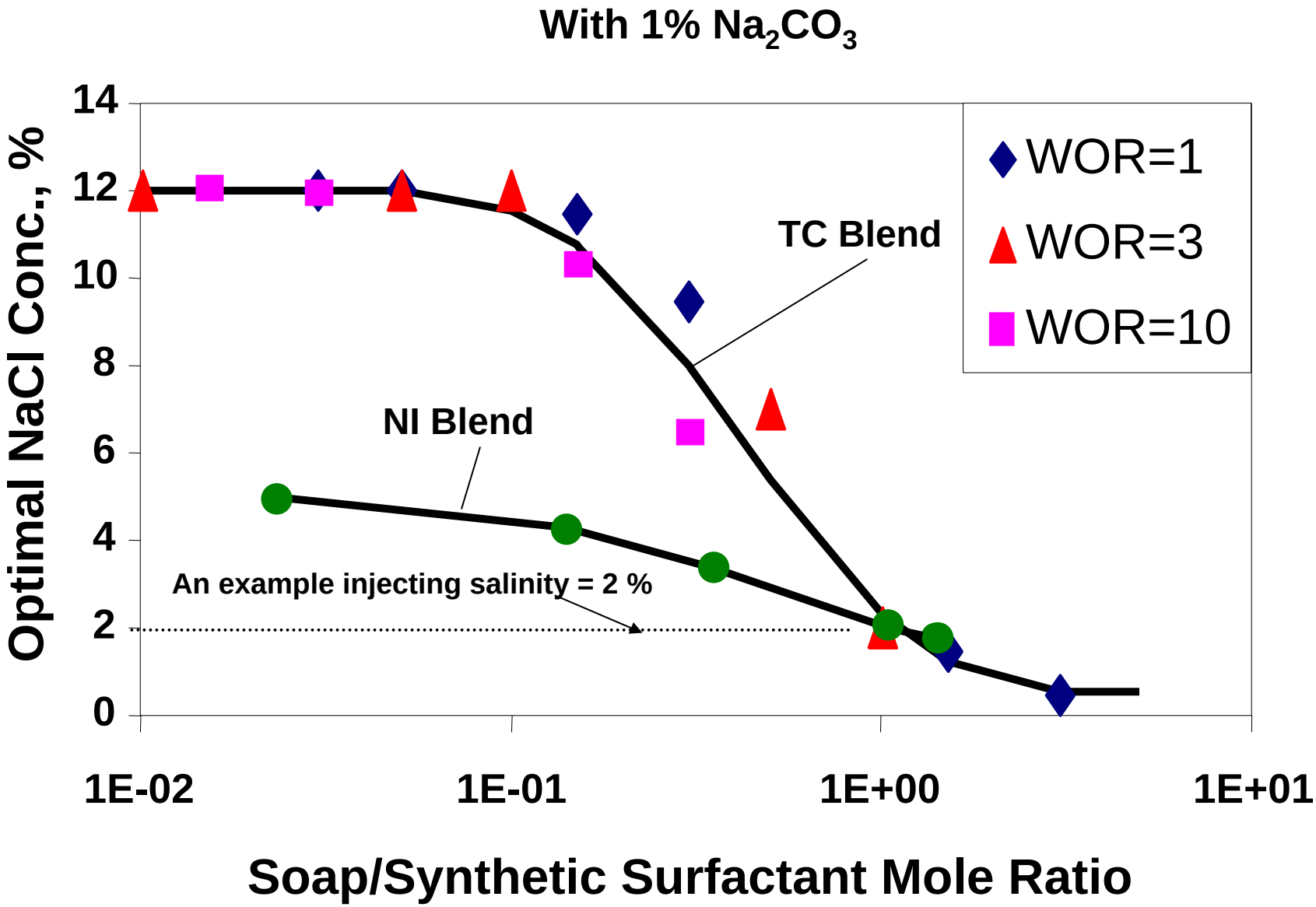
Two Surfactants

Natural Soap (Naphthenic Acid+Alkali)
A hydrophobic surfactant
Generated in situ

Synthetic surfactant
A hydrophilic surfactant
Injected as the surfactant slug


Optimal salinity is a function of water oil ratio (WOR) and surfactant concentration
Surfactant: TC Blend
1% Na2CO3
x% NaCl
Optimal NaCl Conc, %
14
12
10
8
6
4
2
0
0.01
0.1
1
10
Surfactant Concentration, %
WOR=1
WOR=3
WOR=10

Optimal Salinity Correlates with Soap/Synthetic Surfactant Ratio



DESIRED ANIONIC SURFACTANT PROPERTIES FOR ASP PROCESS

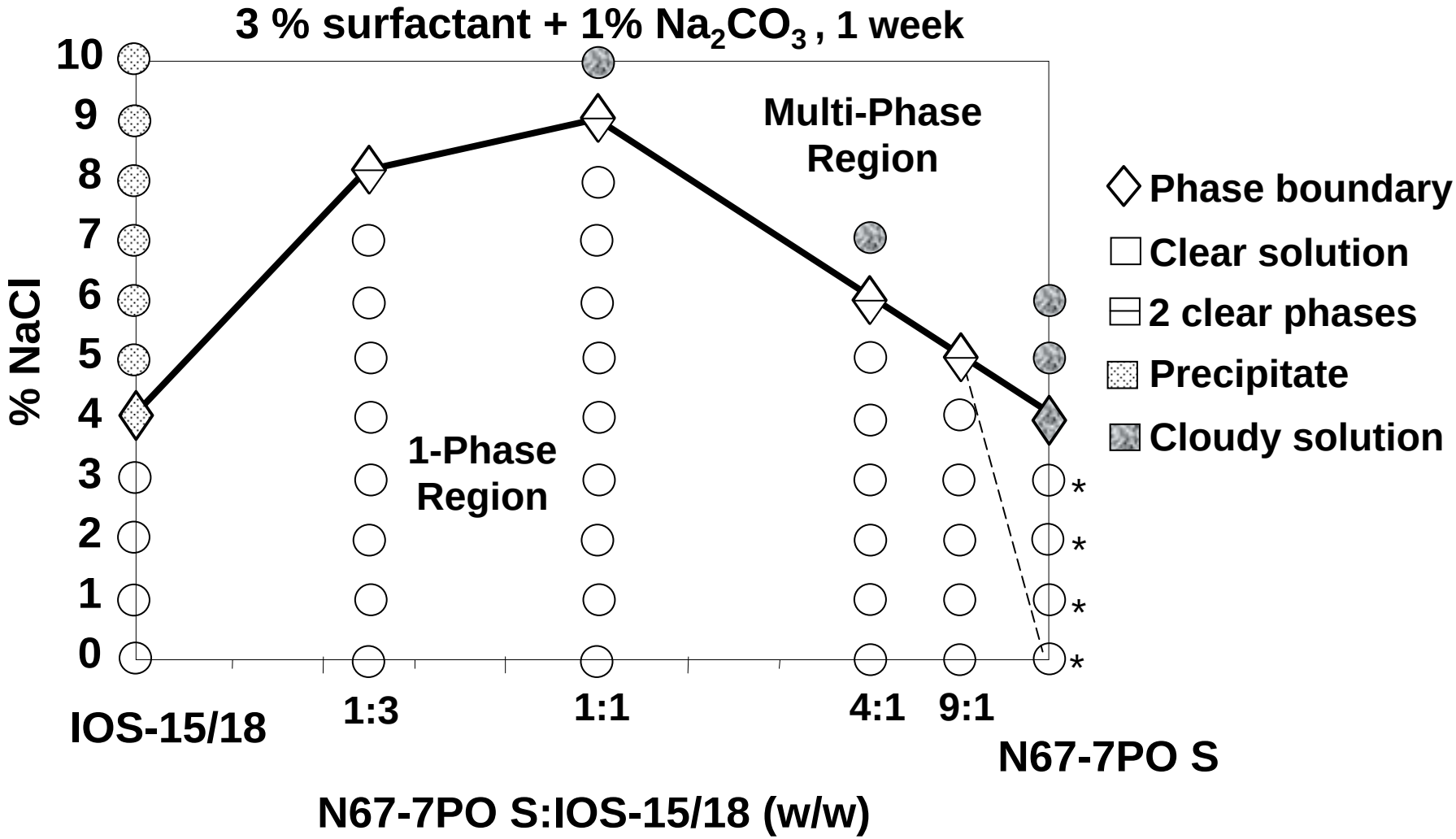
- **Single-phase micellar solution for injection (not true for most petrol. sulfonate/alcohol systems)**
- **Good tolerance of salt and Ca^{+2}, Mg^{+2}; use ethoxylated and/or propoxylated molecules**
- **Branched hydrophobe to minimize viscous phases and emulsions**
- **Ability to displace oil, i. e., achieve low interfacial tensions, over a wide range of conditions**
- **Ability to make oil-wet surfaces more water wet**

SURFACTANT BLEND

- **Neodol 67-7PO Sulfate (N67-7 PO S)**
  C16-17 alcohol with slight branching from Shell; propoxylation and sulfation by Stepan
- **Internal Olefin Sulfonate 15/18 (IOS) from Shell**
  Mixture of species having sulfonate group at various places along hydrocarbon chain
- **NI Blend: 4:1 of N67-7 PO S:IOS 15/18 by weight**
- **No alcohol**

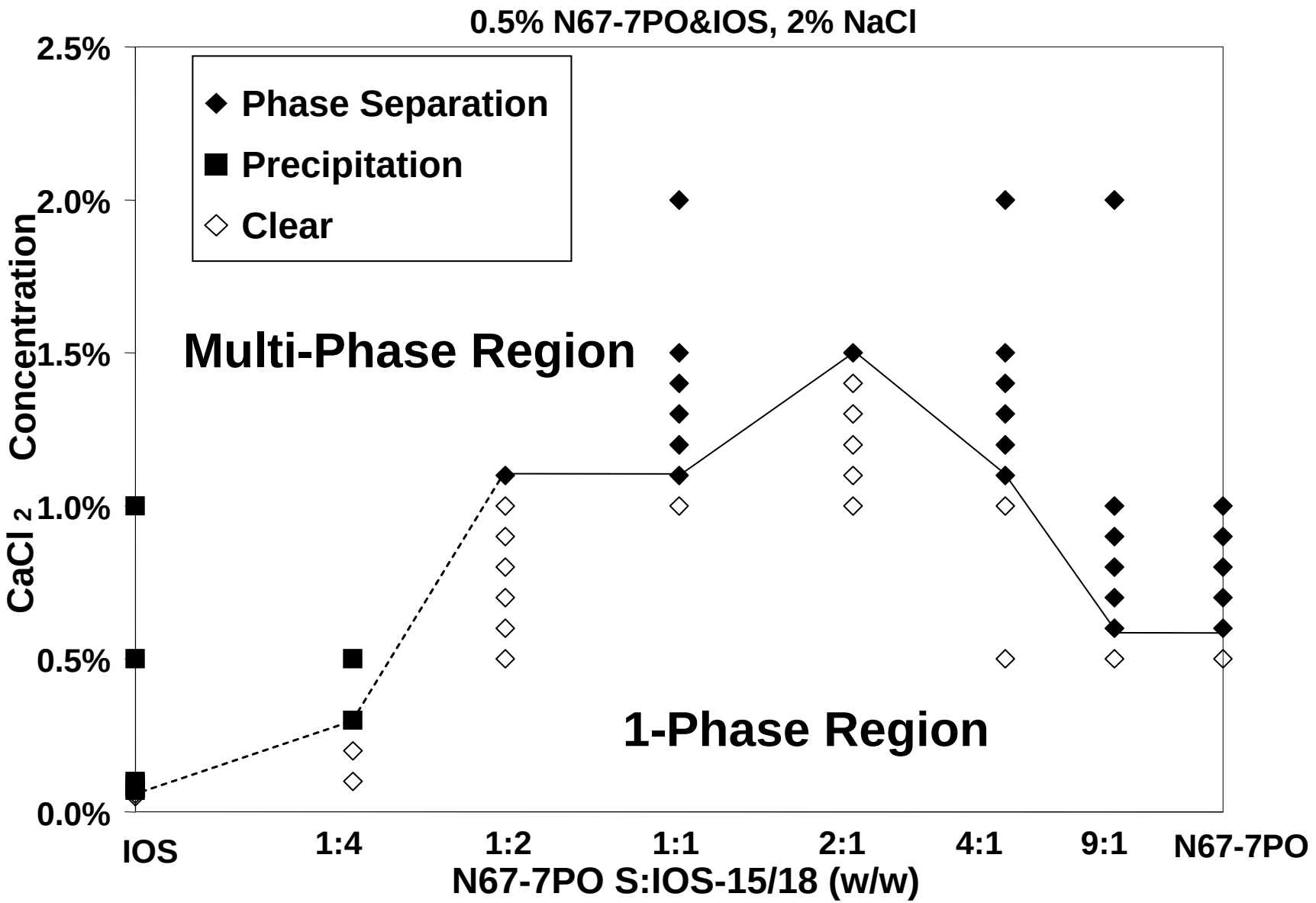
NI Surfactant Blends Improve Salt Tolerance

Surfactant solution should be single phase at injected composition



*** Cloudy after 9 months.**

NI Surfactant Blends Improve Calcium Tolerance

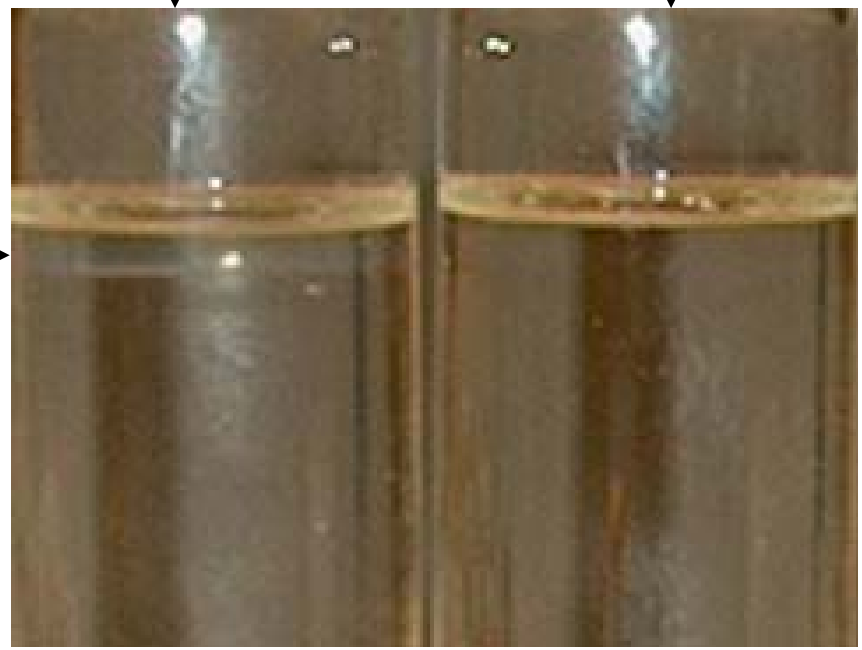


PHASE BEHAVIOR OF ALKALINE/SURFACTANT SLUG WITH ADDED POLYMER (POLYACRYLAMIDE)

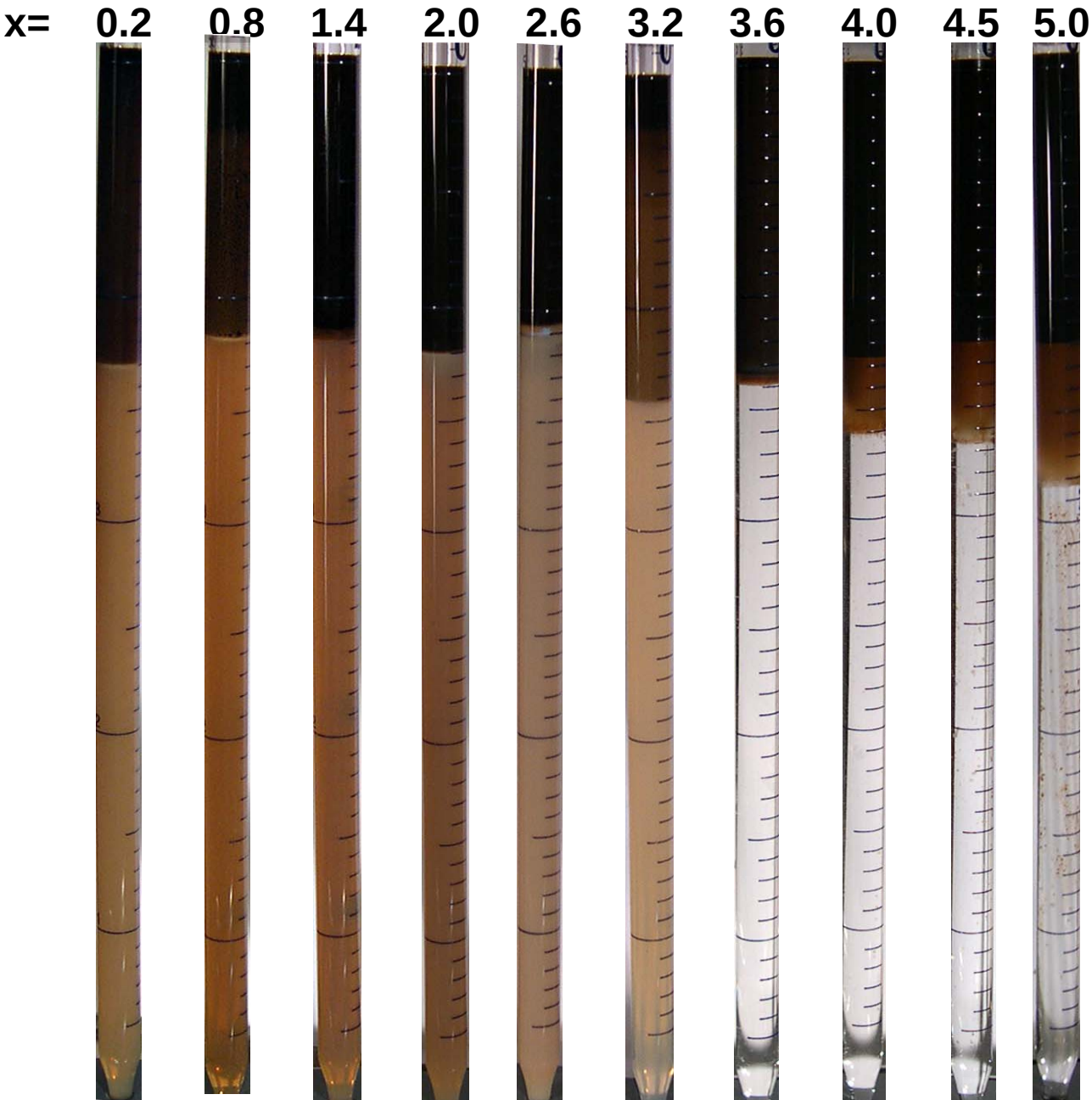
0.5% N67-7PO&IOS(4:1),
0.5% FLOPAM 3330S,
4% NaCl, 1% Na_2CO_3

0.5% N67-7PO&IOS(4:1),
0.5% FLOPAM 3330S,
2% NaCl, 1% Na_2CO_3

Separate layer

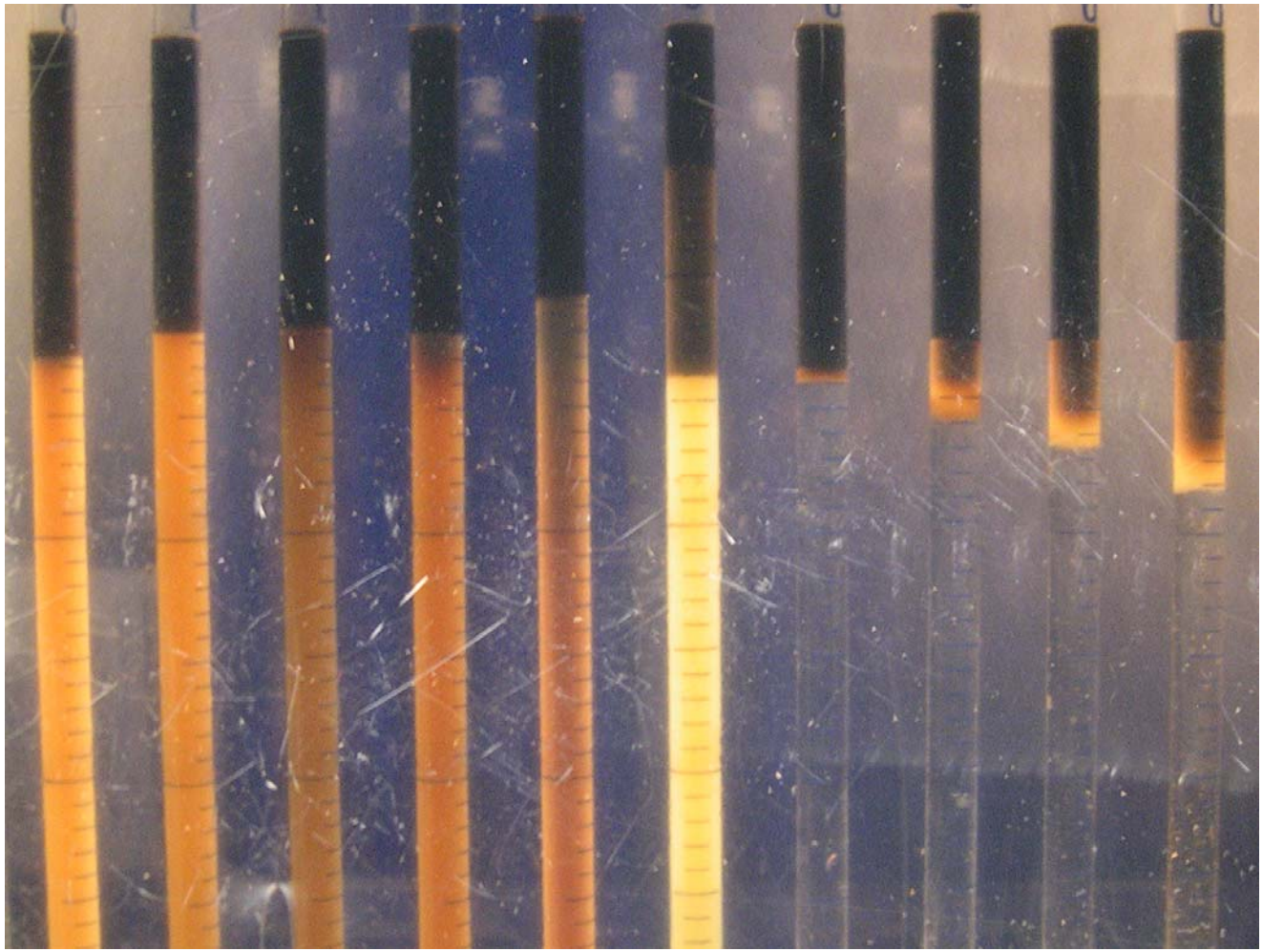


0.2% NI blend / 1% Na_2CO_3 / x% NaCl, WOR=3:1, 24 hours mixing, 28 days settling

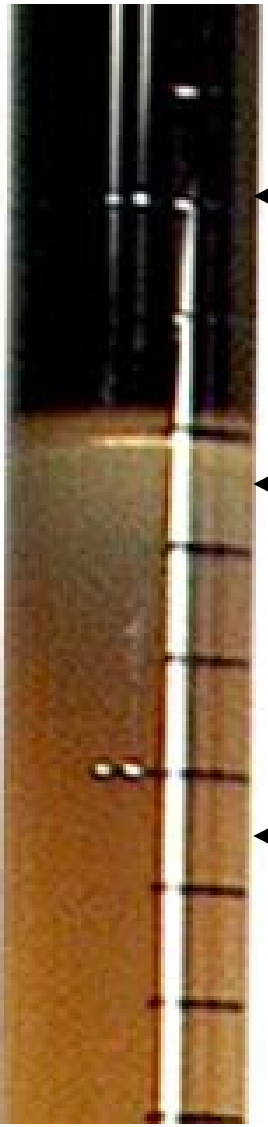


0.2% NI blend / 1% Na_2CO_3 / x% NaCl, WOR=3:1, 24 hours mixing, 28 days settling

x= 0.2 0.8 1.4 2.0 2.6 3.2 3.6 4.0 4.5 5.0



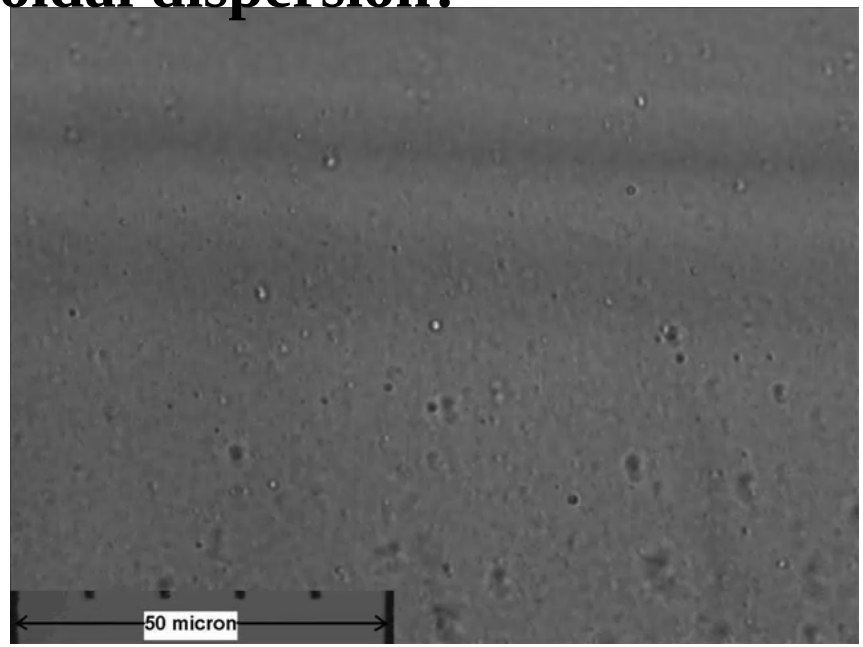
What is the colloidal dispersion?

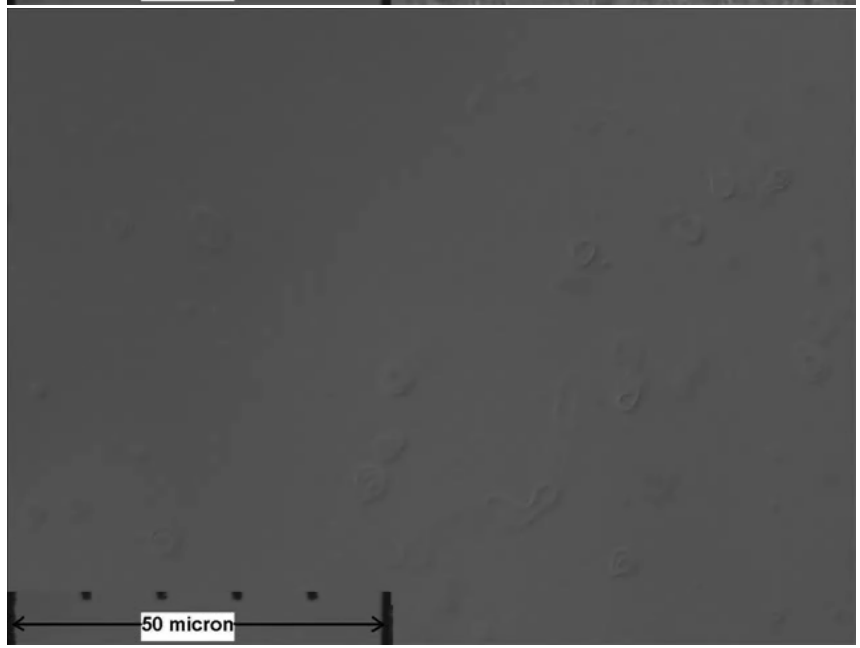


Excess oil

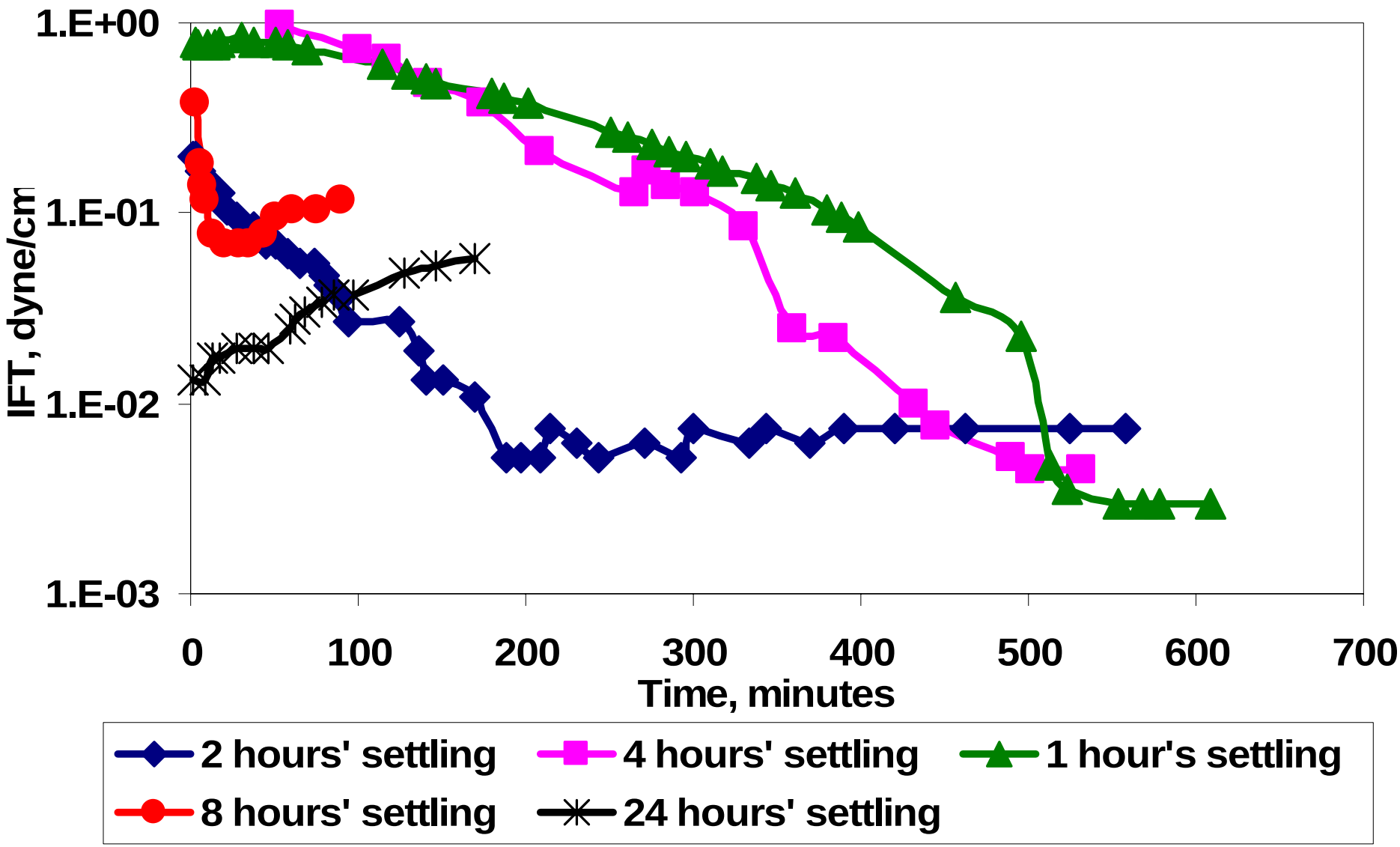
Colloidal dispersion

Lower phase microemulsion





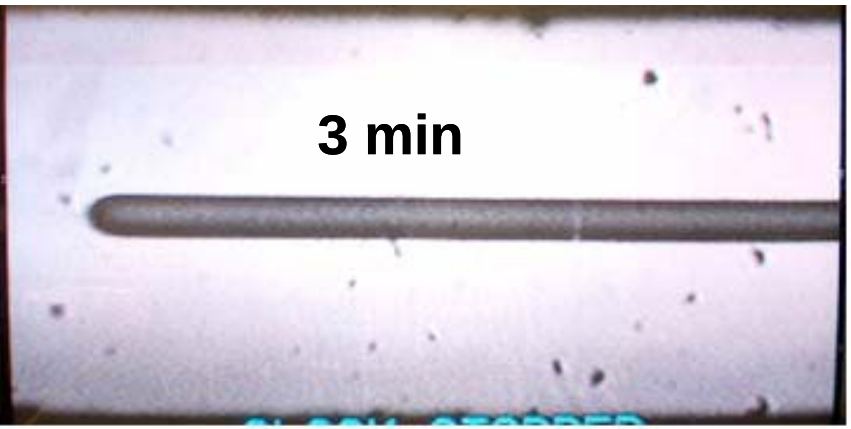
IFT of 0.2%NI-1%Na_2CO_3-2%NaCl vs Settling Time



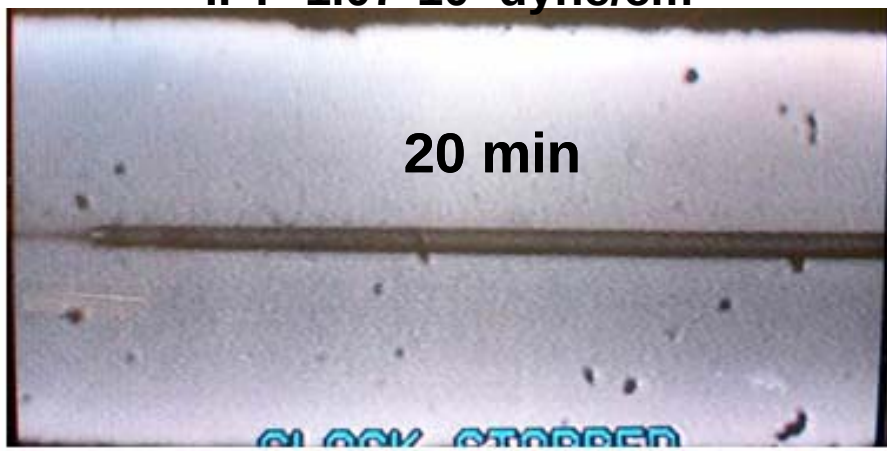
0.2% NI blend /1% Na_2CO_3 / 3.4% NaCl, 23 days settling with colloidal dispersion

fast spinning speed

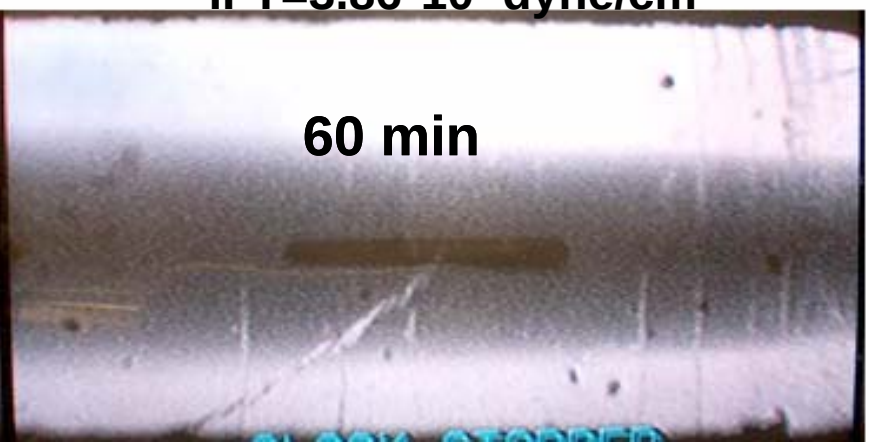
IFT=6.83*10^{-2}dyne/cm



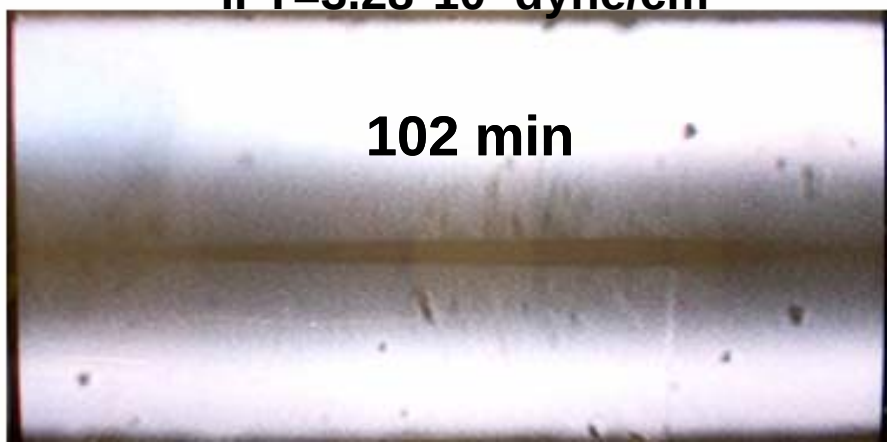
IFT=1.07*10^{-2}dyne/cm



IFT=3.86*10^{-3}dyne/cm

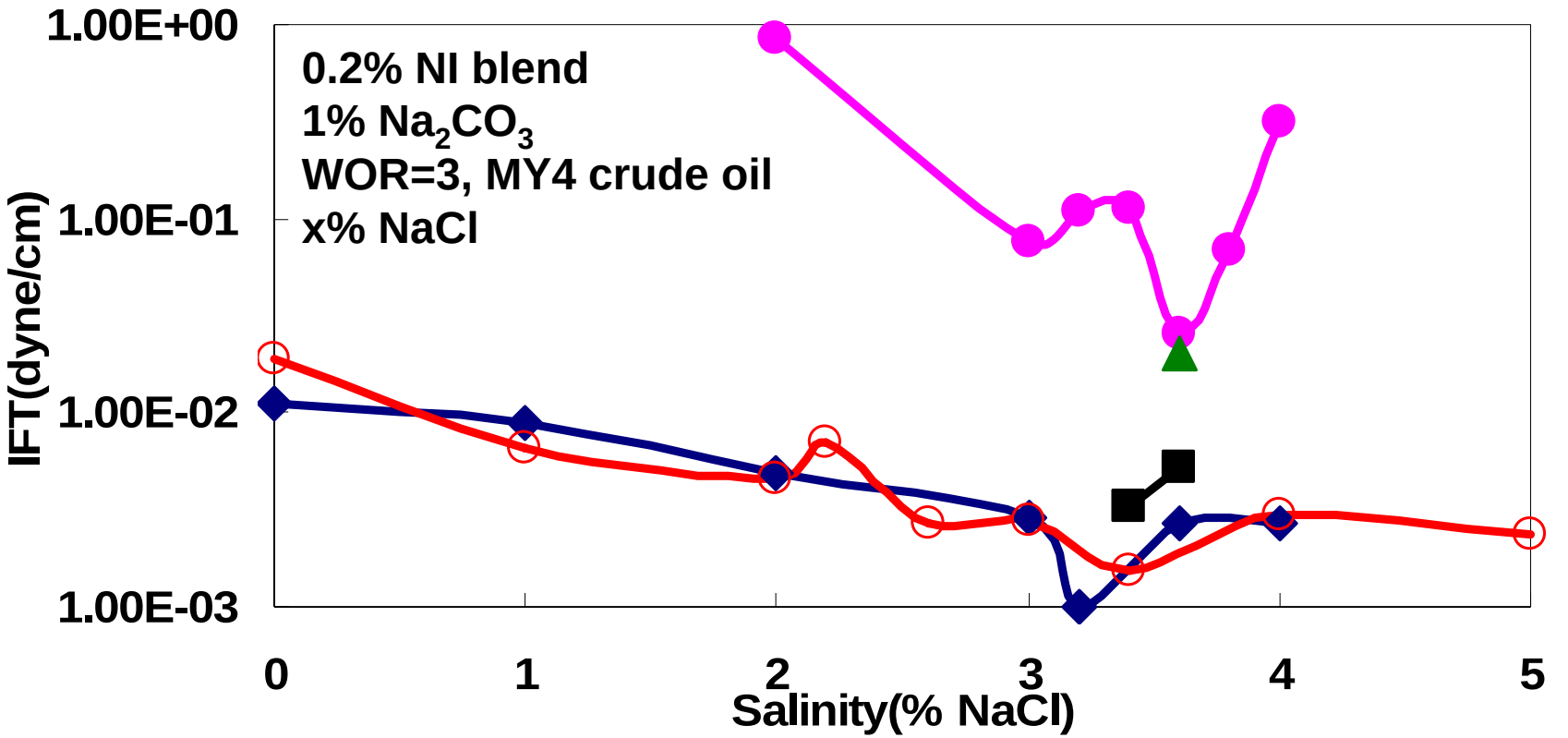


IFT=3.28*10^{-3}dyne/cm



Slow spinning speed

LOW IFT (<0.01 mN/m) OVER WIDE SALINITY RANGE

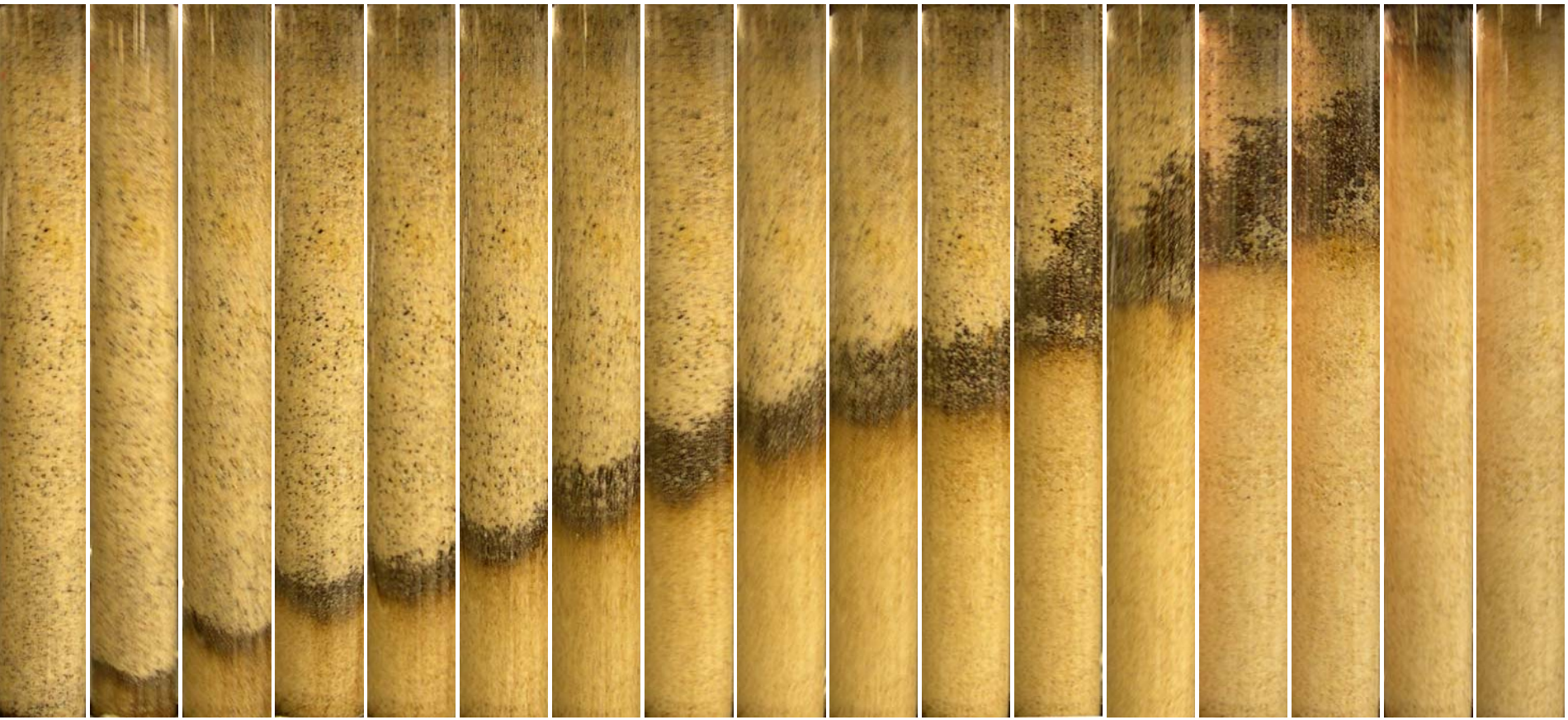


1 day settling & remove all colloidal dispersion by centrifuging
4 hours settling (standard procedure)
4 hours settling (non-standard procedure)
23 days settling
40 days settling

ASP Process

Dolomite sand pack, 35 darcies

0.2% NI, 0.5 PV, 2% NaCl, 1% Na_2CO_3, 5000ppm polymer,MY4 crude oil (19cp)



0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.90 1.50

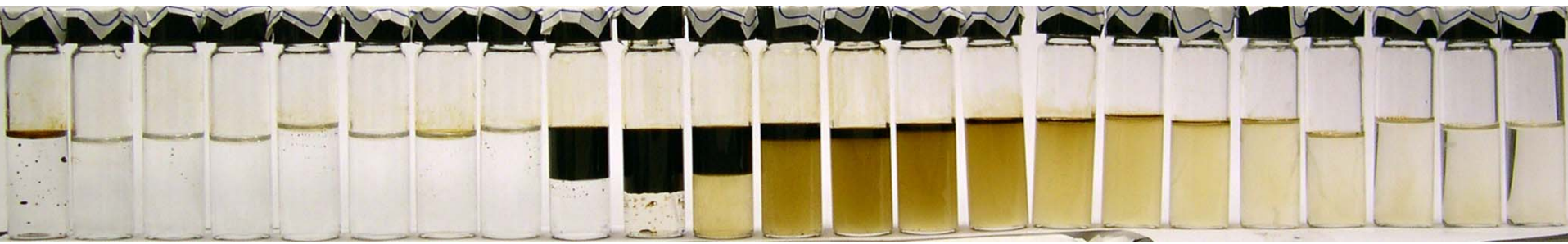
Pore Volumes Injected

EFFLUENT OF ASP FLOOD

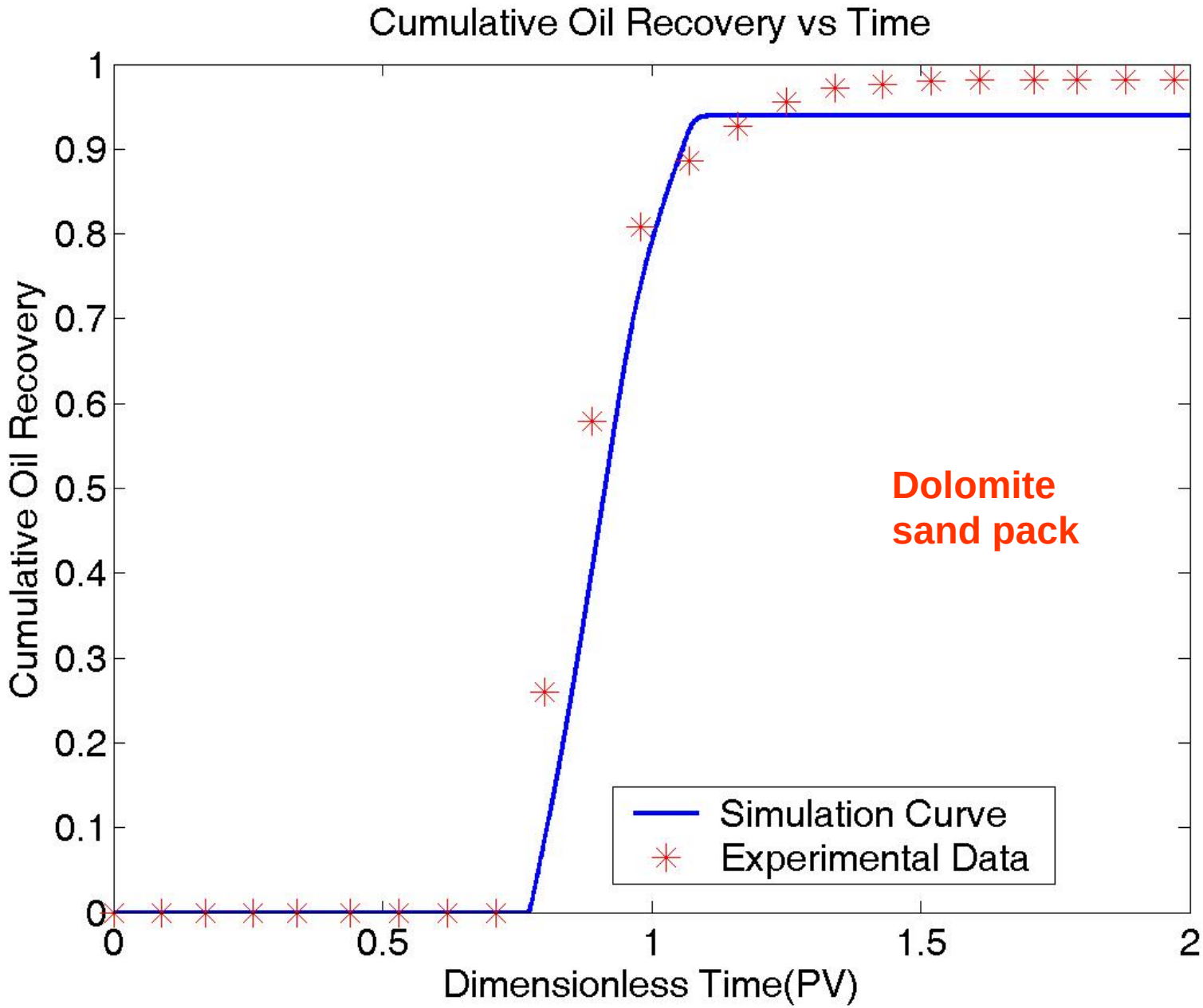
Dolomite sand pack

Effluent Pore Volumes

0.09 0.18 0.27 0.36 0.45 0.54 0.63 0.72 0.81 0.90 0.99 1.08 1.17 1.26 1.35 1.44 1.53 1.62 1.71 1.80 1.89 1.98 2.07

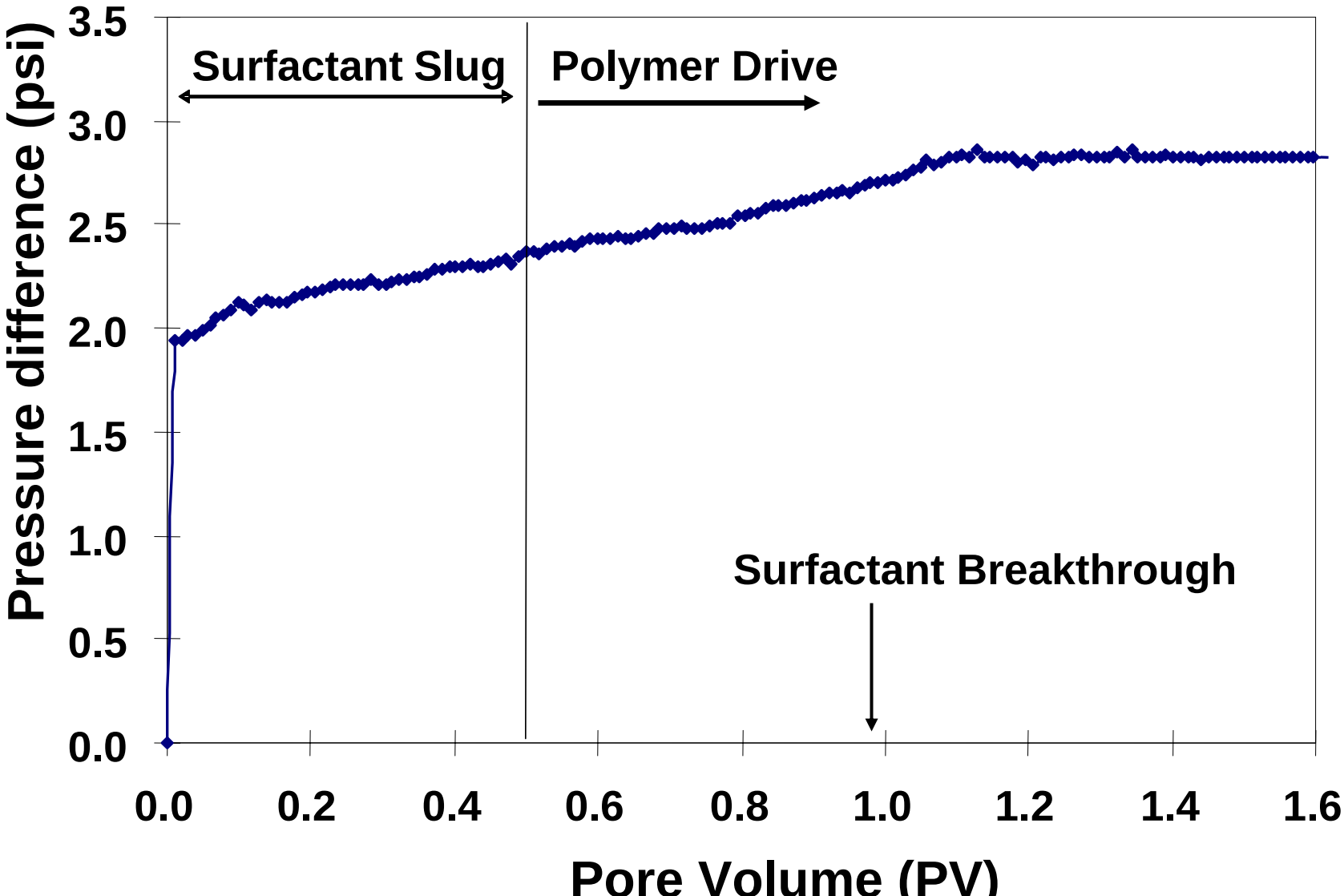


Comparison of Experiment with Simulation



Dolomite
sand pack

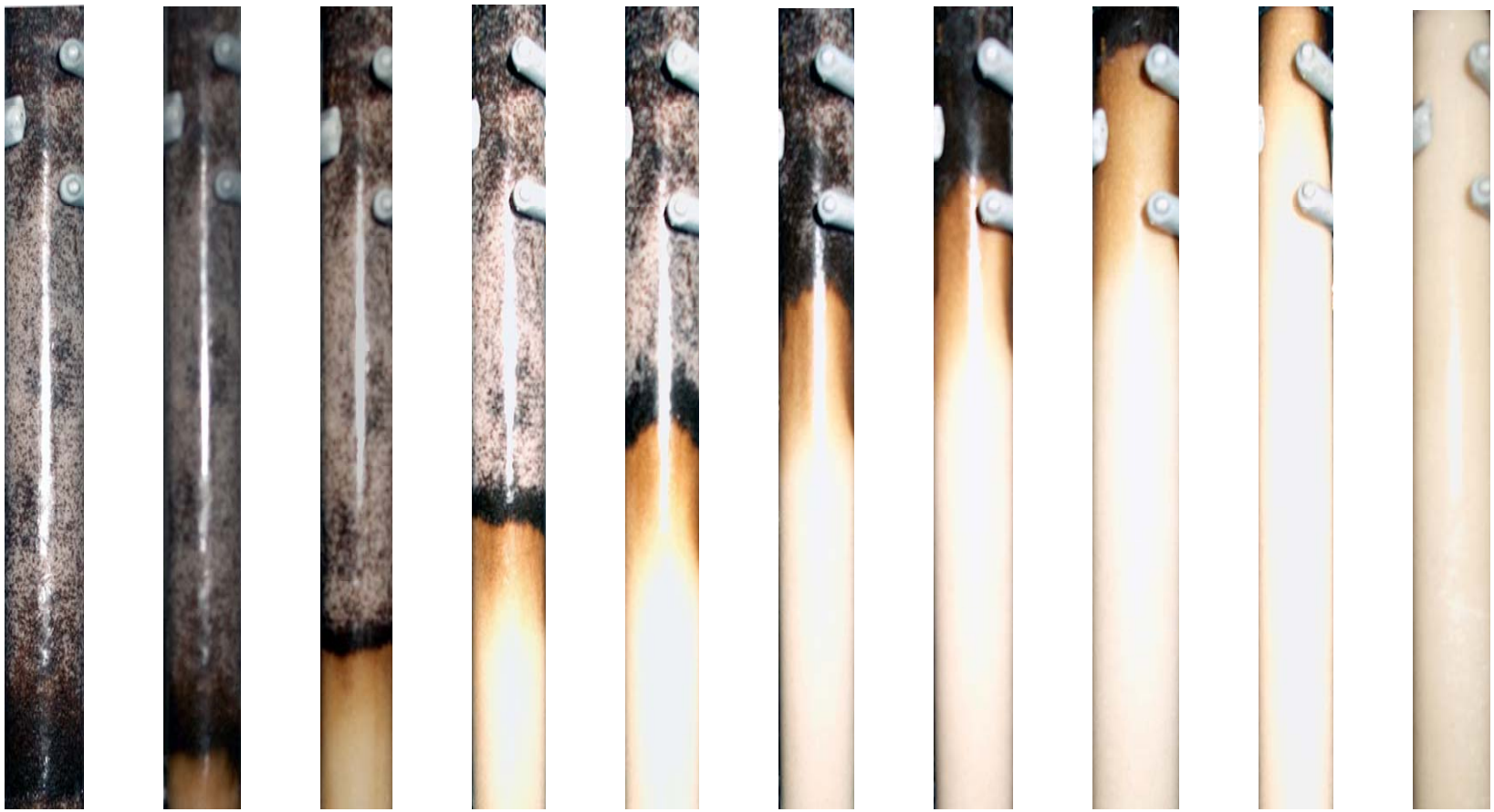
PRESSURE DROP



Silica sand pack

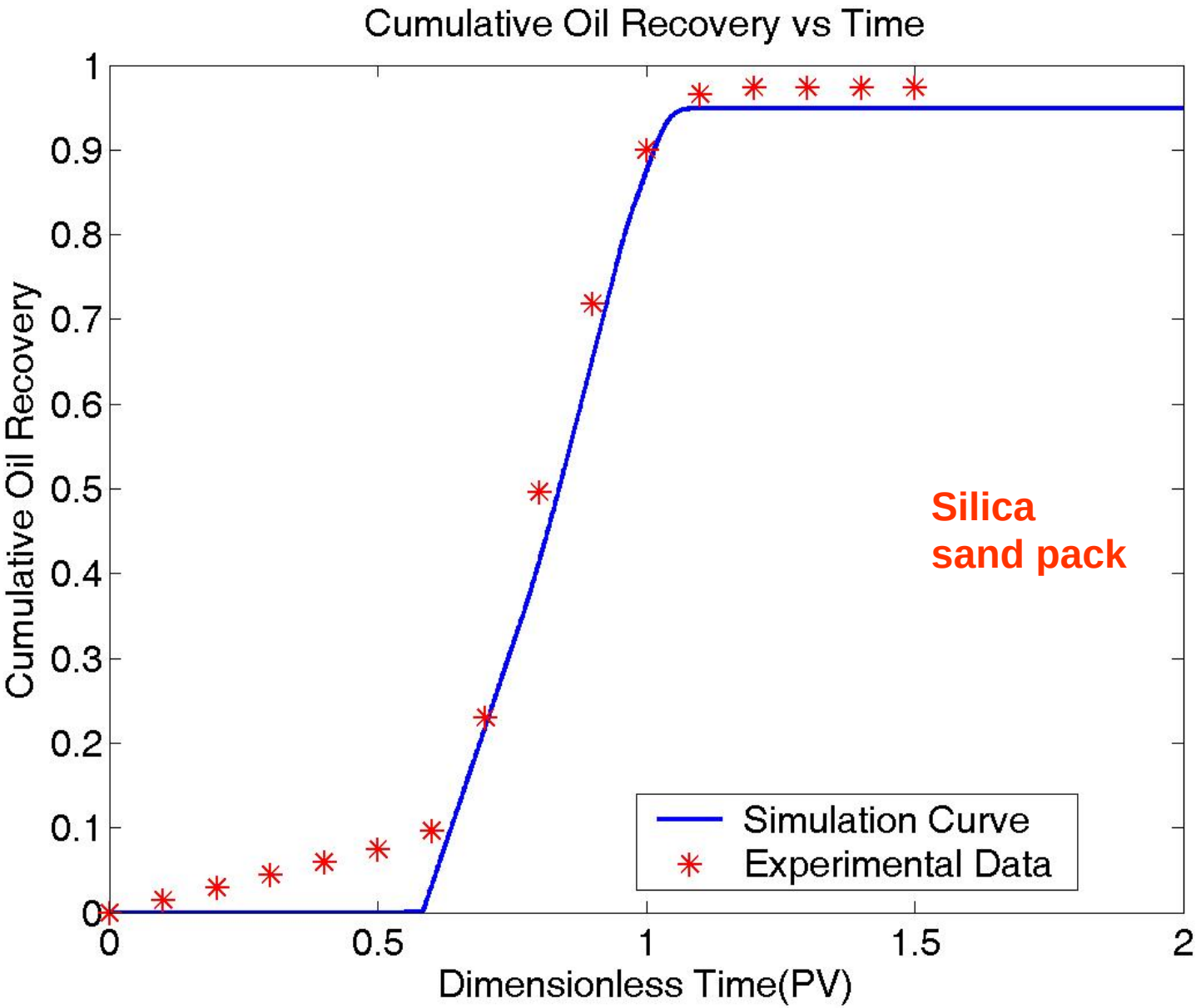
ASP Experiment in 40 darcy Sandpack

0.5% NI, 0.5 PV, 2% NaCl, 1% Na_2CO_3, 5000ppm polymer,MY4 crude oil (19cp)



0 PV 0.1 PV 0.2 PV 0.3 PV 0.4 PV 0.5 PV 0.6 PV 0.7 PV 0.8 PV 1.5 PV

Comparison of Experiment with Simulation

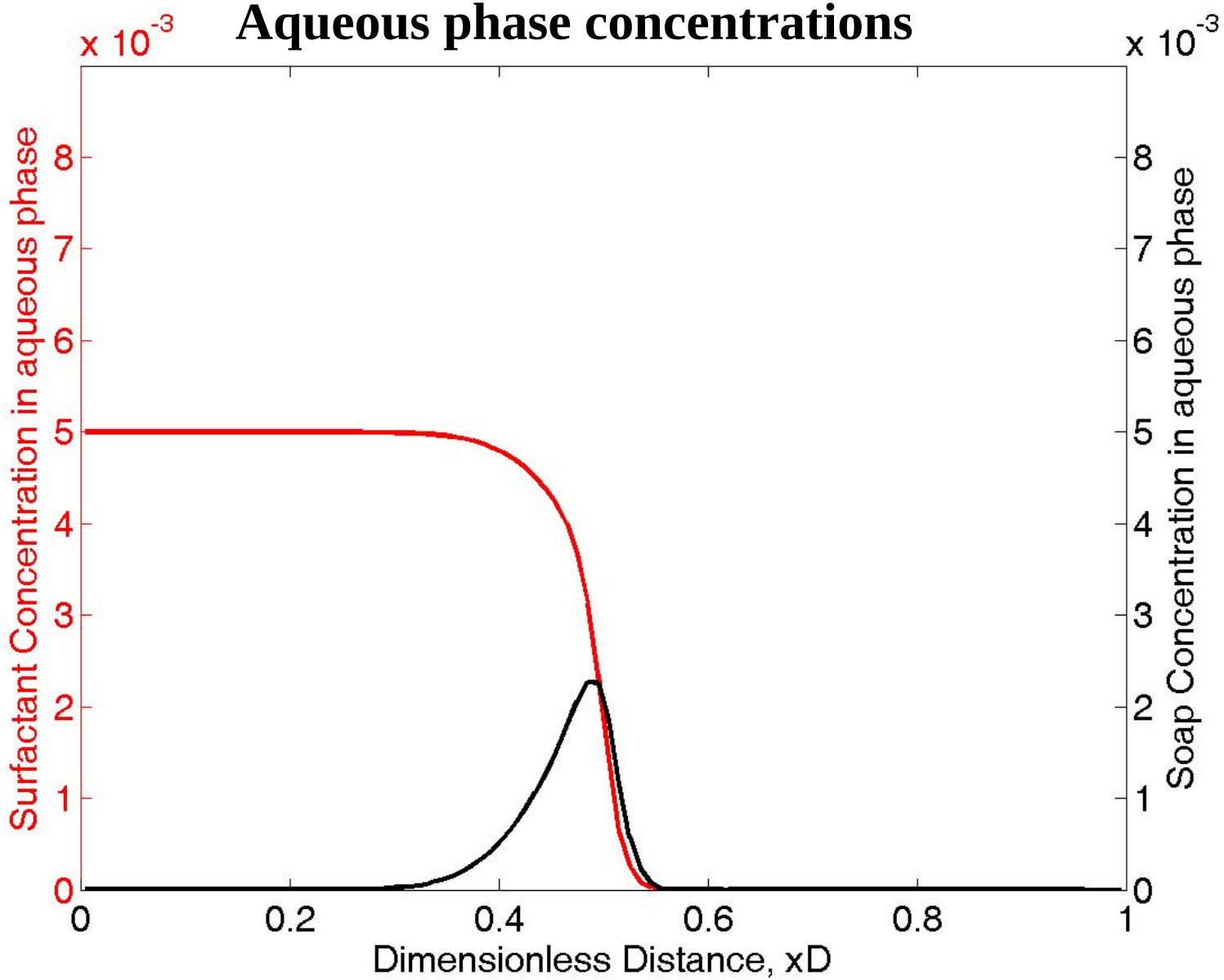


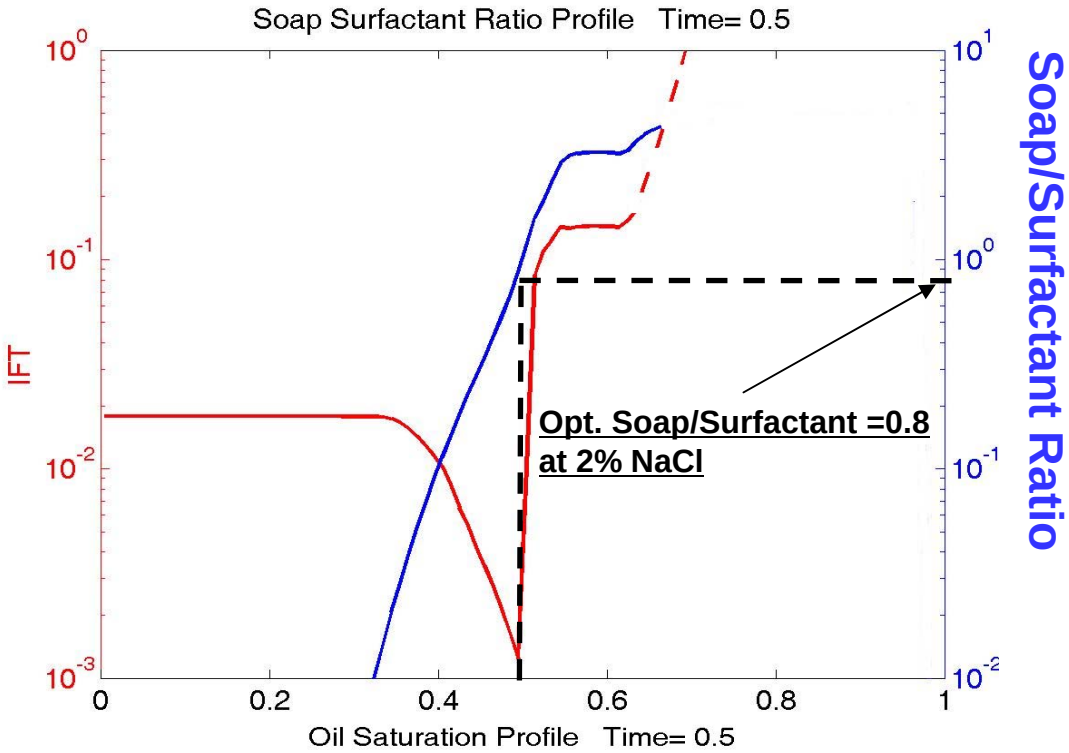
ONE-DIMENSIONAL SIMULATOR

- One- dimensional, two-phase, multicomponent (surfactant, soap, alkali, polymer) finite difference
- Acids in crude oil completely converted to soap by alkali but remain in oil (overoptimum) until surfactant concentration rises sufficiently to produce underoptimum soap/surfactant ratio
- IFT depends on salinity, soap/surfactant ratio; taken below 0.01 mN/m for wide range as per data
- Horizontal displacement; fractional flow curves depend on capillary number
- Include surfactant, polymer adsorption, longitudinal dispersion
- Initial state has S_{or} = 0.30 after waterflood

Composition Profiles at 0.5 PV

Aqueous phase concentrations





Soap/Surfactant (blue) and IFT (red) Profiles, 0.5 PV

Oil Saturation Profiles, 0.5 PV

SIMULATION RESULTS

- **Develop gradient in soap/surfactant ratio; makes process more robust similar to salinity gradient for surfactant flooding**
- **Good oil recovery at salinities well below optimal for synthetic surfactant; get reduced adsorption and no phase separation in slug with polymer**
- **Mobility control is important for high recovery**
- **Wide region of low interfacial tension is needed to achieve oil recovery above 95%**

CONCLUSIONS

- **Na_2CO_3 substantially reduces adsorption of anionic surfactants on carbonates, especially at low salinities**
- **Optimal salinity depends only on soap/surfactant ratio for a given surfactant and crude oil**
- **For 4:1 blend of N67-PO7 S:IOS 15/18 with no alcohol**

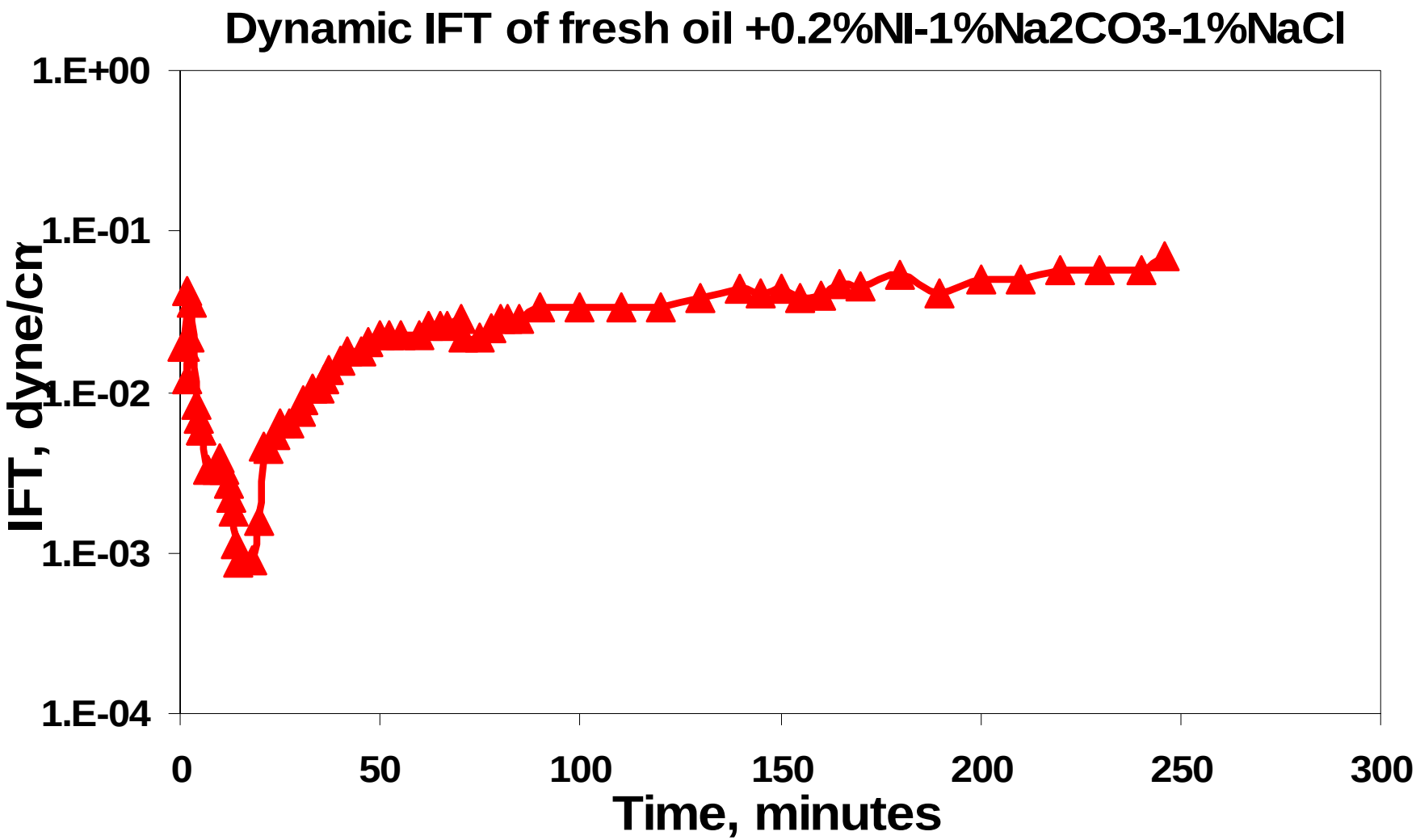
  (a) Single-phase micellar solution at injection conditions

  (b) Colloidal material dispersed in lower phase micro-emulsion is needed to achieve low interfacial tensions

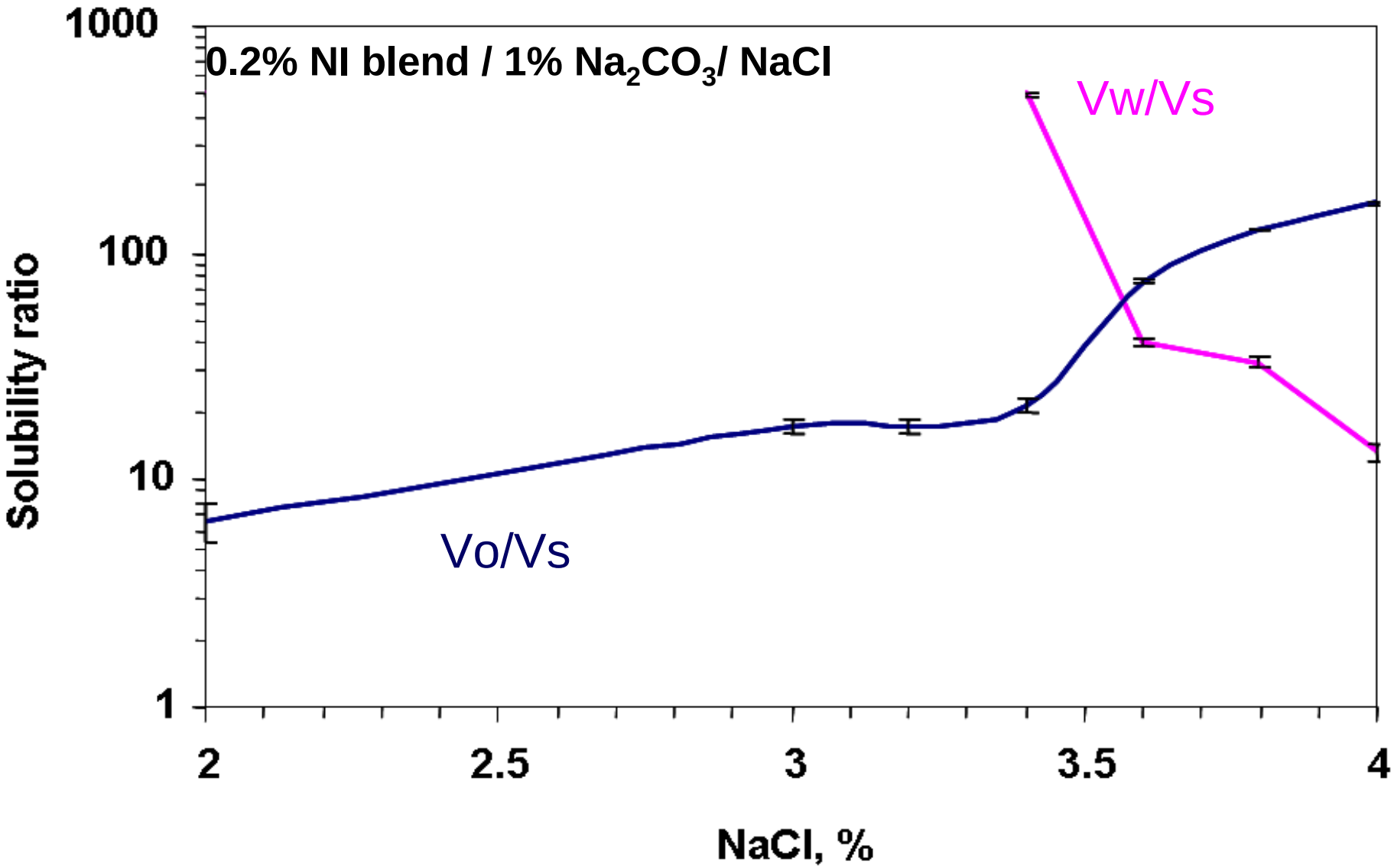
  (c) IFT<0.01 mN/m for wide salinity range; min. IFT=0.001

  (d) Birefringence near the optimal salinity

  (e) ≥95% recovery of West Texas crude oil from dolomite and silica sand packs for ASP process with Na_2CO_3
- **One-dimensional simulator shows robust process with gradient in soap/surfactant ratio, agreement with sand pack recovery curves.**


Dynamic IFT of fresh oil +0.2%NI-1%Na2CO3-1%NaCl
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
IFT, dyne/cm
0
50
100
150
200
250
300
Time, minutes

Solubility Ratios after 30+ days Settling Indicate Low IFT



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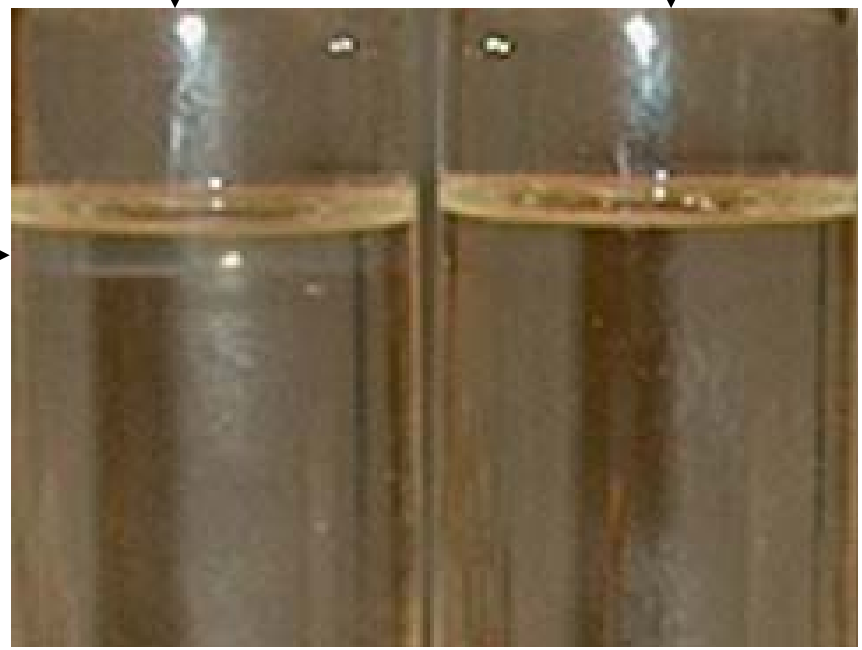
Separate layer



Silica sand pack

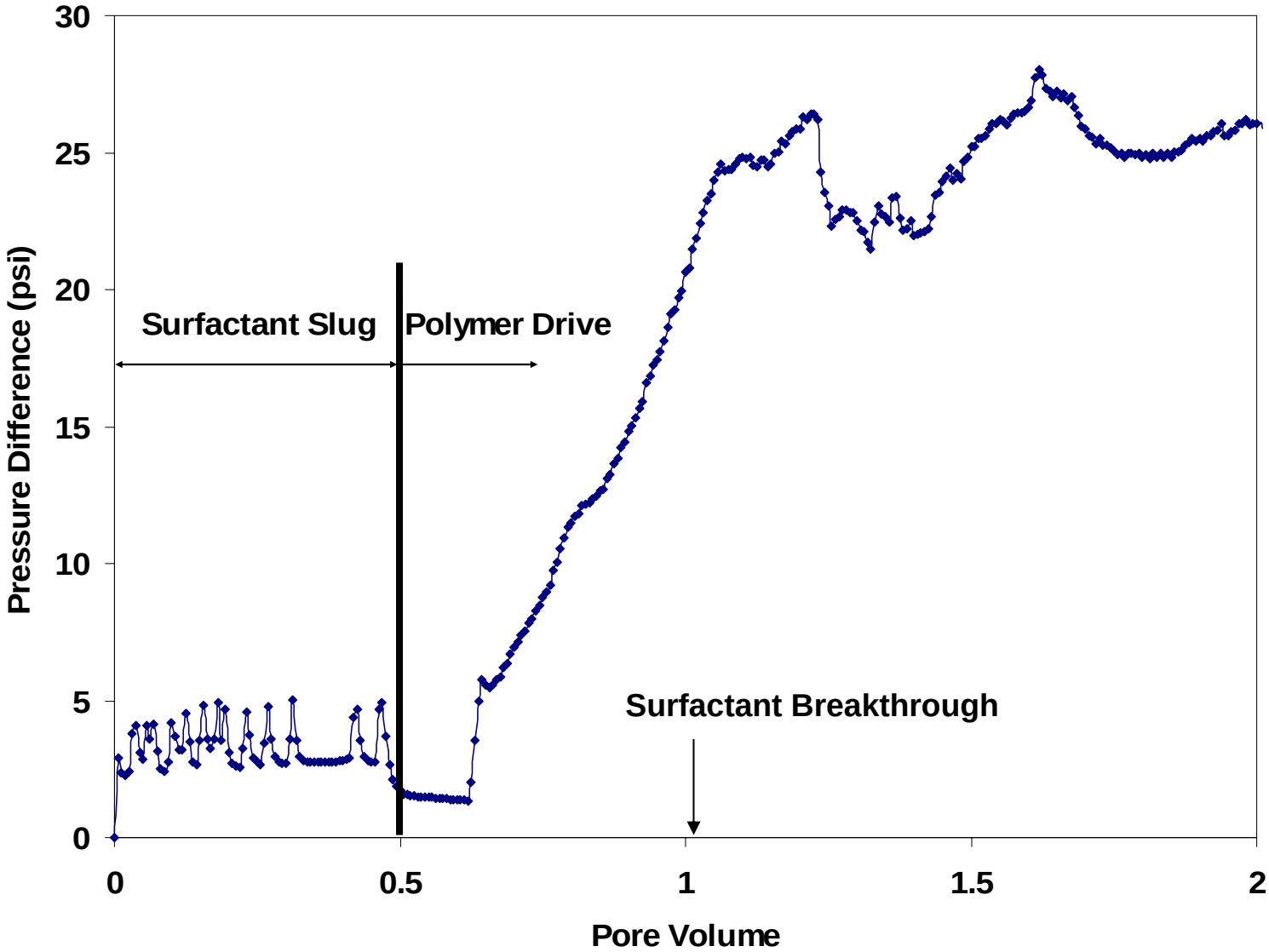
ASP Experiment in 40 darcy Sandpack

0.5% NI, 0.5 PV, 4% NaCl, 1% Na_2CO_3, 5000ppm polymer,MY4 crude oil (19cp)

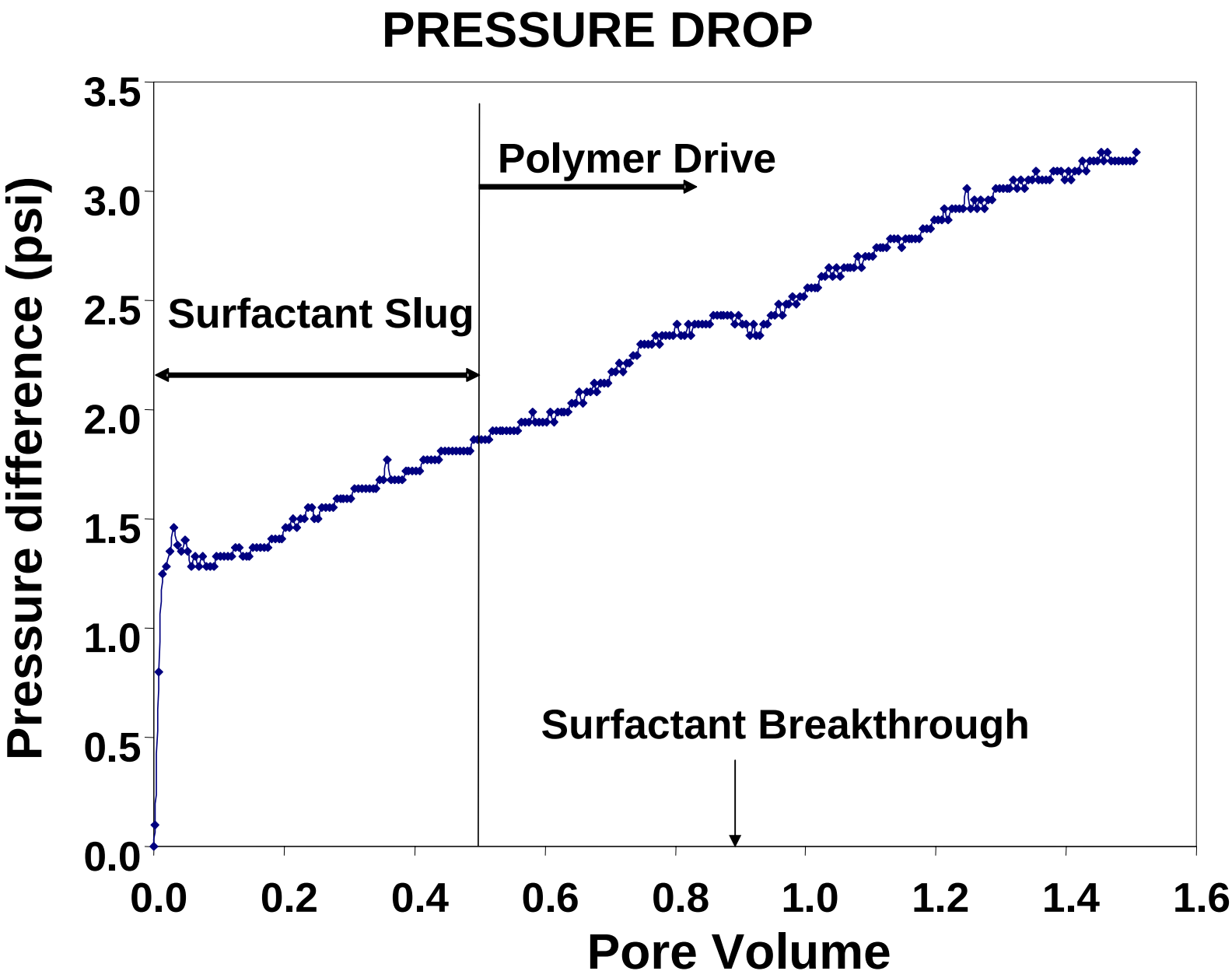
0 PV | 0.17 PV | 0.33 PV | 0.5 PV | 0.67 PV | 0.83 PV | 1.0PV | 2.0 PV

Silica
sand pack

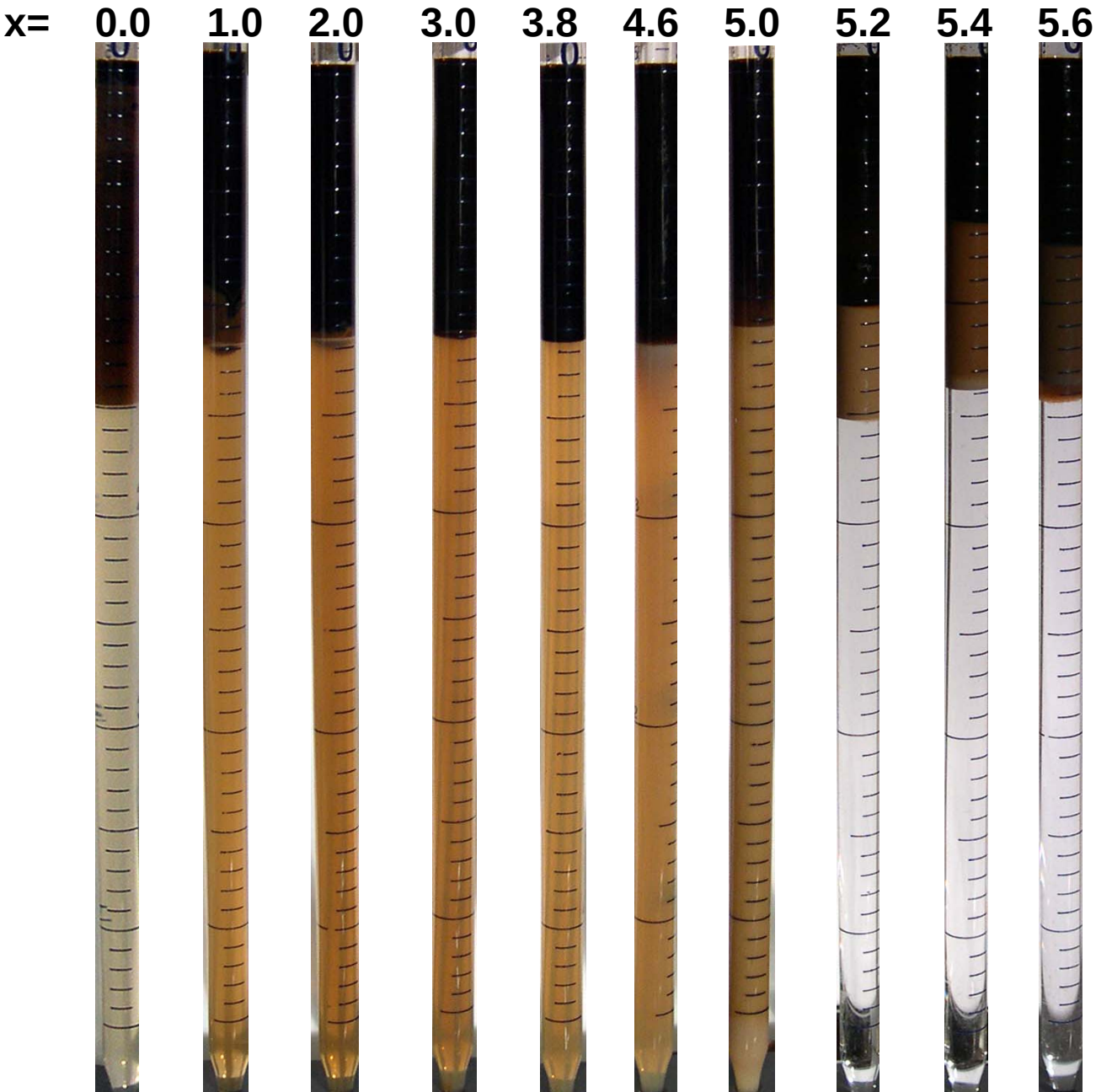
Excess pressure drop begins at the polymer drive



Silica
sand pack



0.2% NI blend / 0% Na_2CO_3 / x% NaCl, WOR=3:1, 24 hours mixing, 28 days settling



0.2% NI blend / 0% Na_2CO_3 / x% NaCl, WOR=3:1, 24 hours mixing, 28 days settling

x= 0.0 1.0 2.0 3.0 3.8 4.6 5.0 5.2 5.4 5.6